

Pecan shell-based granular activated carbon for treatment of chemical oxygen demand (COD) in municipal wastewater

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Abstract

The present investigation was undertaken to compare the adsorption efficiency of pecan shell-based granular activated carbon with the adsorption efficiency of the commercial carbon Filtrasorb 200 with respect to uptake of the organic components responsible for the chemical oxygen demand (COD) of municipal wastewater. Adsorption efficiencies for these two sets of carbons (experimental and commercial) were analyzed by the Freundlich adsorption model. The results indicate that steam-activated and acid-activated pecan shell-based carbons had higher adsorption for organic matter measured as COD, than carbon dioxide-activated pecan shell-based carbon or Filtrasorb 200 at all the carbon dosages used during the experiment. The higher adsorption may be related to surface area as the two carbons with the highest surface area also had the highest organic matter adsorption. These results show that granular activated carbons made from agricultural waste (pecan shells) can be used with greater effectiveness for organic matter removal from municipal wastewater than a coal-based commercial carbon.

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1. Introduction

Activated carbon is carbon treated at high temperature with a physical or chemical activating agent producing an internal porous particle structure and has been used for many years in wastewater treatment. Activated carbons can be divided into two main classes: those used for adsorption of gases and vapors for which a granular activated material is usually employed, and those in purification of liquids for which a powdered material is desired. Granular activated carbons (GACs) are used in the form of a carbon bed, usually within a column, for water treatment. The water flows through the bed, where organic molecules present as contaminants are adsorbed on to the carbon surface. When the carbon is saturated with the adsorbed molecules, the carbon loses its adsorptive ability, and is removed from the system and regenerated.

Many carbonaceous materials, such as petroleum coke, sawdust, lignite, coal, peat, wood, charcoal, nut-shell, and fruit pits, may be used for the manufacture of activated carbon, but the properties of the finished material are governed not only by the raw material, but also by the method of activation used. The choices of raw material are based upon the end use of the activated carbon, availability, cost of the raw material, and national and international economic and political considerations. For instance, decolorization of sugar involves the use of powdered activated carbon. Raw material for the production of powdered carbon can be non-renewable material such as coal but also can be agricultural by-products with a soft structure, such as rice straw, sugarcane bagasse, soybean hulls, sawdust, or peanut shells. Vapor adsorbent carbons are used in the form of hard granules and generally granular activated carbons (GACs) are made from either coal or imported coconut shells, an agricultural by-product with a very hard structure.

Abundance and low cost of US agricultural by-products, especially tree nut shells, make them good

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candidates as precursors for granular activated carbon (Toles et al., 1997, 1998, 1999; Johns et al., 1998, 1999). The US produced 178 million lbs of pecans in crop year 2002 (Agricultural statistics, 2003). Production and processing of this commodity generated about 89 million lbs of pecan shells as a by-product.

In recent years, there has been an increasing awareness of the limited water resources. This recognition has led to the concept of water reuse rather than disposal. Acceptance of the concept of reuse has been accelerated by the development of new wastewater treatment processes that can economically yield clean, high quality water. One such process is the adsorption of wastewater contaminants by activated carbon treatment.

A comprehensive review of the literature has shown that there is a need in wastewater treatment plants to find economically affordable alternatives to activated carbons made from US coal or imported coconut shells that are becoming more expensive and in short supply, especially coconut shells. Our earlier work was oriented toward the use of nutshell-based granular activated carbons for adsorption of volatile organic compounds (Bansode et al., 2003; Johns et al., 1998, 1999), and non-volatile organic compounds, such as geosmin (Ng et al., 2002a,b). The present investigation is a continuation of our work in establishing these carbons for adsorption of non-volatile organic compounds that comprise the chemical oxygen demand (COD) in municipal wastewater. It is anticipated that this work would provide a comprehensive guide for the municipal wastewater treatment plants in understanding the role of the agriculture-based granular activated carbons for the removal of different contaminants present in municipal wastewater.

This study was undertaken to compare the adsorption efficiencies of pecan shell-based carbons with respect to organic matter measured as COD to the adsorption efficiency of a commercial carbon, Filtrasorb 200, in municipal wastewater from Baton Rouge, LA. A comparison of adsorption efficiencies for these two sets of carbons (experimental and commercial) was carried out and analyzed by the Freundlich adsorption model. As far as we are aware, this study describes the first use of nutshell-based carbons for the adsorption of organic matter defined as COD.

2. Materials

The commercial carbon, Filtrasorb 200 (F-200), was obtained from Calgon Carbon Corp., Pittsburgh, PA. Filtrasorb 200 is a coal-based, commercially available activated carbon mainly employed in municipal wastewater treatment plants for removal of organic as well as inorganic contaminants. The COD test vials were procured from HACH (Loveland, CO). Primary treated municipal wastewater was collected from the Central

Municipal Processing Plant at Baton Rouge, La. The wastewater was filtered using Whatman #4 filter paper to remove suspended particles and used immediately after filtration.

3. Methods

3.1. Preparation of granular activated carbons

Pecan shells were milled to a 10×20 mesh size (US standard sieve) with a cross-beater mill (Glen Mills, Clifton, NJ). Milled samples were placed in a box furnace with retort (Lindberg, Watertown, WI). For steam or carbon dioxide activation, the pecan shells were initially pyrolyzed under a stream of nitrogen gas at a flow rate of 0.1 m³/h and a pyrolysis temperature of 700 °C for 1 h. Steam activation involved injecting water into the nitrogen gas flow (0.1 m³/h) entering the heated retort at a flow rate of 2 ml/min at an activation temperature of 900 °C for 6 h. A yield of 14% of the initial mass of shells was obtained. Carbon dioxide activation required exposing the pyrolyzed shells to a gas mixture of 30% carbon dioxide and 70% nitrogen (wt/wt) at an activation temperature of 900 °C for 6 h. A yield of 22% of the initial shell mass was recorded. After activation, the carbons were cooled overnight in the retort under a nitrogen gas atmosphere and were ready for use.

For phosphoric acid activation, the milled pecan shells were soaked with 50 wt.% phosphoric acid for 2 h. The soaked shells were heated in a flowing nitrogen gas environment inside the retort at a flow rate of 0.1 m³/h and at a temperature of 170 °C for 1 h. The nitrogen gas was replaced with compressed air and introduced into the retort at the same flow rate as the temperature was increased to 450 °C and held at this temperature for 1 h. The compressed air was used for concurrent oxidation and chemical activation. Earlier studies indicated that 370–410 °C was the upper threshold temperature where pecans shell-based granular activated carbon experience excessive mass loss to oxidative burn-off during air exposure (Johns et al., 1998).

The acid activated carbons were cooled overnight in the retort, then washed in boiling water until free of detectable phosphate ion as evidenced by the lack of a lead phosphate precipitate upon introduction of a few drops of lead nitrate to a sample of the wash water. The washed carbons were dried at 102 °C for at least 2 h before use. A yield of 39% was determined for the pecan shell carbons.

3.2. Measurement of physical and chemical properties of activated carbons

Surface areas for all carbons were measured by nitrogen adsorption at 77 K using a Micromeritics

Gemini 2375 surface area analyzer (Micromeritics Inc., Norcross, GA) using a 15 point BET (Brunauer et al., 1938). Bulk density was determined using the method of Ahmedna et al. (1997). A 25 ml cylinder was filled to a specified volume with 10–30 mesh granular activated carbons that had been dried in an oven at 80 °C overnight. The cylinder was tapped for at least 1–2 min to compact the carbon, and then weighed. The bulk density was calculated as:

Bulk density (g ml^{-1})

$$= [\text{wt of dry material (g)} / \text{vol of packed dry material (ml)}]$$

Carbon hardness was determined using a wet attrition test as described by Toles et al. (2000). Ten to 30 mesh (1.00–0.65 mm) carbons were used. One g of GAC was added to 100 ml of acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid, pH 4.8) in a 150 ml beaker. The solution was stirred for 24 h at 25 °C on a Variomag Electronic Ruhrer Multipoint HP 15 stirrer (Daytona Beach, FL) at 500 rpm using 1/2 in. stir bars. The samples were then poured onto a 50 mesh (0.30 mm) screen, and the retained carbon was washed with 250 ml of deionized water. After washing, the retained carbon was transferred to a preweighed, aluminum weighing dish and dried at 90 °C under vacuum for 4 h. The samples were removed and allowed to cool in a desiccator and weighed. The attrition (% attrition) was calculated as:

%attrition

$$= [\text{initial wt (g)} - \text{final wt (g)}] / [\text{initial wt (g)}] \times 100$$

Ash content (% ash) was determined by the method of Ahmedna et al. (1997). Approximately 2 g of powdered activated carbon was placed into weighed ceramic crucibles. Carbon and crucibles were dried overnight at 80 °C and reweighed to obtain the dry carbon weight. The samples were heated in a Jetrus 250 muffle furnace (Hicksville, NY) at 1400 °F (760 °C) for at least 6 h. The crucibles were cooled in a desiccator, and remaining solids (ash) were weighed. Percent ash was calculated by:

$$\% \text{ash} = [\text{remaining solids wt (g)} / \text{original carbon wt (g)}] \times 100$$

The pH was measured using the method of Ahmedna et al. (1997). A 1% (wt/wt) suspension of activated carbon in deionized water was prepared. The suspensions were heated to approximately 90 °C and stirred for 20 min. The suspensions were then allowed to cool to room temperature and the pH was measured with a Corning pH 10 portable pH meter (Acton, MA). The pH meter was initially calibrated with pH 4 and pH 7 buffers. If the pH was found to be above pH 7, the pH meter was recalibrated with pH 7 and pH 10 buffer solutions. The calibration was confirmed by analysis of a pH 7 buffer after every five analysis, and a recalibration done if the

value of the pH 7 buffer varied by more than ± 0.1 pH unit.

Conductivity measurements were carried out by the method of Ahmedna et al. (1997). A 1% (wt/wt) solution of GAC in water was stirred at room temperature for 20 min. Electrical conductivity was measured using a HACH CO 150 Conductivity Meter (Loveland, CO) with values given in microSiemens (μS).

3.3. Chemical oxygen demand (COD)

The granular activated carbons were milled in a ball mill (Spex 8000 mixer/mill, Metuchen, NJ) to a particle size to <325 mesh (<45 μm). Particles this small would eliminate particle size as the rate-limiting step for adsorption (Randtke and Snoeyink, 1983). Different carbon dosages ranging from 0.01 to 1.5 g per 100 ml of wastewater were used for this study. Adsorption was carried out for 2 h. After adsorption, the samples were filtered using a 0.45 μm PTFE filter, and the filtered samples were stored at 4 °C until analyzed for residual COD levels, where COD is a measure of the oxygen required to degrade the organic matter present in wastewater.

The COD of the wastewater treated with experimental and commercial activated carbons were determined by a colorimetric method (5220D) recommended by the Standard Method for Examination of Water and Wastewater (Clesceri et al., 1998). The test method consisted of the use of HACH test vials containing dichromate reagent as a chemical oxidant for measuring COD in the range of 0–1500 mg/l.

3.4. Statistical analysis

Analysis of variance with a 95% confidence level ($\alpha = 0.05$) and Tukey's multiple comparison test were done on duplicate determinations of each sample to determine the significant difference between the physical and chemical properties among various carbons using SAS 8.0 software (SAS, 1989).

4. Results and discussion

4.1. Physical and chemical properties of the GACs

The experimental results obtained on the physical properties (total surface area, bulk density and attrition), chemical properties (pH, ash content, conductivity) of the pecan shell-based GACs and the commercial carbon are presented in Table 1. The values for both the physical and chemical properties of the experimental carbons were similar to the values reported by Ng et al. (2002a). This would be anticipated considering both sets

Table 1

Physical and chemical properties of experimental and commercial granular activated carbons

Property	Carbon			
	PSA	PSC	PSS	F-200
Surface area (m ² /g)	902 ± 4 ^{a,b,d}	435 ± 39 ^{a,c,d}	917 ± 5 ^{b,c,d}	835 ± 10 ^{a,b,c}
Bulk density (g/cm ³)	0.51 ± 0.00 ^b	0.57 ± 0.00 ^{a,c,d}	0.49 ± 0.00 ^b	0.49 ± 0.00 ^b
Attrition (%)	7.10 ± 0.45 ^{a,b,d}	12.8 ± 0.1 ^{a,c,d}	22.2 ± 1.0 ^{b,c,d}	3.26 ± 0.07 ^{a,b,c}
Ash (%)	1.42 ± 0.01 ^{a,b,d}	6.00 ± 0.08 ^{c,d}	5.53 ± 0.16 ^{c,d}	6.57 ± 0.03 ^{a,c}
pH	5.70 ± 0.52 ^{a,b}	10.1 ± 0.0 ^c	10.0 ± 0.2 ^c	7.40 ± 0.78 ^{a,b,c}
Conductivity (μm)	46.0 ± 0.3 ^{a,b,d}	331 ± 0 ^{a,c,d}	753 ± 3 ^{b,c,d}	5.85 ± 0.35 ^{a,b,c}

F-200 = Filtrasorb 200 (Calgon Carbon Corp.), PSC = pecan shell-based carbon dioxide-activated carbon, PSS = pecan shell-based steam-activated carbon, PSA = pecan shell-based acid-activated carbon.

^a Significantly different than PSS ($\alpha = 0.05$).

^b Significantly different than PSC ($\alpha = 0.05$).

^c Significantly different than PSA ($\alpha = 0.05$).

^d Significantly different than F-200 ($\alpha = 0.05$).

of carbons were produced by the methods of Ahmedna et al. (2000).

Among the three pecan shell-based carbons, steam activation (PSS) produced the largest total surface area at 917 m²/g, followed by acid activation (PSA) at 902 m²/g, and carbon dioxide activation (PSC) produced the lowest total surface area at 435 m²/g. The commercial carbon, Filtrasorb 200 (F-200), had a total surface area of 835 m²/g. The results seem to indicate why acid and steam activation are preferred activation methods as commercial processes compared to carbon dioxide activation. Carbon dioxide is more expensive than steam, in addition to yielding a lower surface area under the same activation conditions of time and temperature.

The data in Table 1 indicate that bulk density was higher for the carbon dioxide and acid activated carbons than for the commercial carbon. All experimental carbons had bulk densities equal to or greater than F-200. The results (Table 1) indicate that the commercial carbon displayed significantly lower attrition than the nutshell based carbons. Normally, the starting material can influence the attrition of the final carbon. In this case, bituminous coal, used as the starting material for F-200, may be harder than the pecan shells used for the experimental carbons. Also, attrition can be a function of carbon surface area whereby a carbon can possess such high surface area that part of its internal structure is weakened, resulting in high attrition. In the present case, the highest attrition was found in the carbon (PSS) with the greatest surface area.

Ash content was lowest in the PSA carbon (Table 1). Unwashed PSA carbons have high ash contents (>10%) due to the presence of excess phosphoric acid. Extensive water washing in this case reduced the ash content to 1.42%. Ahmedna et al. (2000) showed that water washing of carbons made from acid-activated pecan shells reduced the percent ash levels to 2.2%. However, in some cases values as high as 6.0% ash were also reported for the water wash treatment. The physically

activated, pecan shell carbons had higher ash contents (5.53–6.00%) than the acid-activated carbon, as they did not undergo any wash procedures after activation. Percent ash values of 1.6–3.2% have been observed for physically activated, pecan shell carbons that have undergone a water wash (Ahmedna et al., 2000). Therefore, water washing can reduce carbon ash content to lower values than found in the unwashed samples. The ash content of the PSS and PSC carbons in the present case probably reflects the ash content of the pecan shell starting material.

The pH values show representation of acidic, neutral and alkaline carbons (Table 1). Chemical activation produced an acid carbon (pH of 5.7) and the commercial carbon (F-200) was essentially neutral with a pH of 7.4. Physical activation resulted in basic carbons with a pH of 10. The basic nature of these carbons is probably due to the presence of ash components, such as magnesium, associated with the carbon. The high conductivity of these basic carbons (Table 1) also points to the presence of metal ions resulting from the ash fraction. An acid wash of the physically activated carbons would remove the ash fraction, lower conductivity and reduce the pH closer to 7.0.

5. Adsorption of organic matter measured as COD

5.1. Effect of carbon dosage on COD of test solution

The effect of carbon dosage ranging from 0.0 to 1.5 g of carbon/100 ml of solution on organic matter adsorption of the test solution is presented in Fig. 1. The initial COD concentration of the untreated municipal wastewater ranged from 40.0 to 66.5 mg/l and the corresponding pH was 7.55. Therefore, each adsorption curve (Fig. 1) had a slightly different COD starting concentration. Different initial concentrations could have a small but undetermined effect on the % COD removed (Fig. 1).

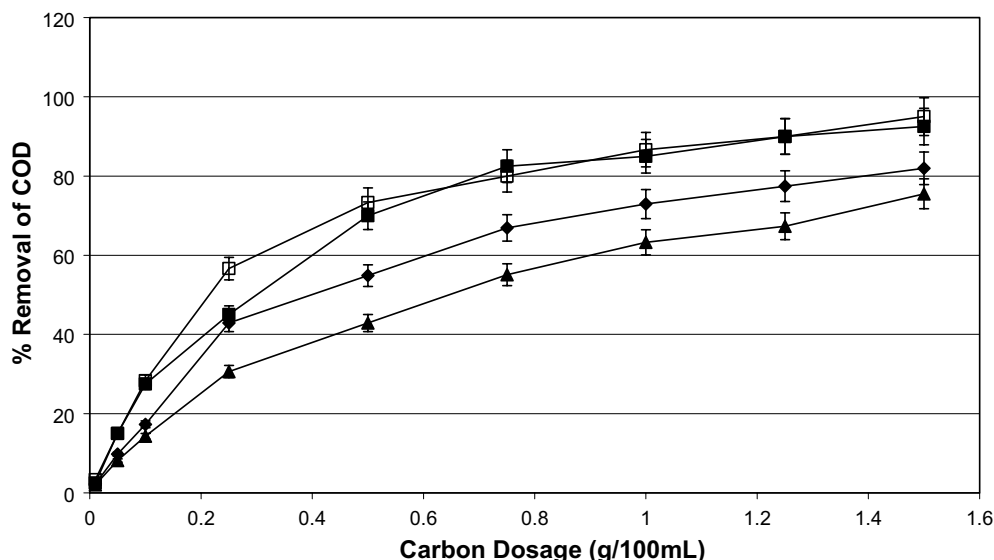


Fig. 1. Percentage removal of Chemical oxygen demand (COD) by experimental and commercial powdered activated carbons. The symbols used were: (◆) F-200—Filtrisorb 200, (■) PSS—pecan shell-based steam-activated carbon, (▲) PSC—pecan shell-based carbon dioxide-activated carbon, (□) PSA—pecan shell-based acid-activated carbon.

The data presented in Fig. 1 indicate that the steam-activated and acid-activated carbons had higher adsorption with respect to organic matter (measured as COD) than the carbon dioxide-activated carbon and F-200. This was true throughout the range of the carbon dosages used. A comparison of the performance of steam- and acid-activated carbons indicates similar adsorption efficiency over the entire carbon dosage range.

These observations indicate that adsorption of the organic component in the wastewater are related to carbon surface area. Acid- and steam-activated carbons possessed similar surface areas (Table 1), which were the highest of the four samples. F-200 had intermediate adsorption properties and intermediate surface area. Carbon dioxide-activated pecan shells were lowest in both organic adsorption efficiency and surface area.

5.2. Application of Freundlich model to organic matter adsorption measured as COD

Adsorption isotherms are a graphical representation showing the quantity of adsorbate adsorbed by a unit weight of adsorbent. Adsorption isotherms describe the thermodynamics of adsorption and are used to describe adsorption equilibria that may require long contact times for compounds that adsorb only slowly (Huang et al., 1996). It also provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently a carbon will adsorb and allows an estimate of the economic feasibility of the carbons commercial application for the specified solute (Ng et al., 2002a). These isotherms can be described based on

various theoretical models, Freundlich isotherms equation being the most commonly used because of its utility in describing adsorption data, especially adsorption data at low adsorbate concentrations (Ng et al., 2002a; Huang et al., 1996).

Adsorption isotherms can be generated based on numerous theoretical models where the Langmuir and Freundlich models are the most commonly used. The Langmuir model is the simplest model that can be used to describe monolayer adsorption based on a kinetic approach and assumes a uniform surface, a single layer of adsorbed material and constant temperature (Ng et al., 2002b). Adsorption isotherms expressed as the Freundlich model have been found to be a better measure of the adsorptive properties of activated carbons and are based on the distribution of solute between the activated carbon (solid phase) and aqueous phase at equilibrium. The Freundlich model is suitable for use with the heterogeneous surfaces for a single solute system, an assumption made in our experiment with respect to the organic matter in municipal wastewater system. The basic Freundlich equation is:

$$x/m = kC_e^{1/n} \quad (1)$$

where x is the amount of COD adsorbed; m , weight of carbon; x/m , concentration of COD adsorbed per carbon dosage; C_e , equilibrium concentration of COD in solution; k and $1/n$ are constants.

A linear form of the Freundlich equation is represented by:

$$\log(x/m) = \log k + 1/n \log C_e$$

The data on the effects of carbon dosage on the organic adsorption of the test medium were fitted to a

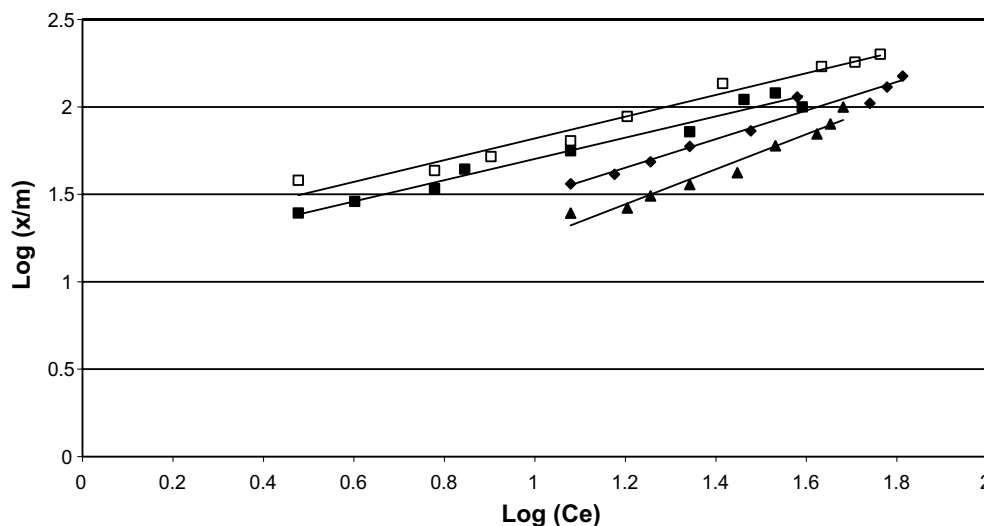


Fig. 2. Adsorption isotherms for the adsorption of chemical oxygen demand (COD) by pecan shell-based and commercial activated carbon using the Freundlich adsorption model. The symbols used were: (◆) F-200—Filtrisorb 200, (■) PSS—pecan shell-based steam-activated carbon, (▲) PSC—pecan shell-based carbon dioxide-activated carbon, (□) PSA—pecan shell-based acid-activated carbon.

Freundlich model, and graphical representations of this model are presented in Fig. 2. The respective constants k and $1/n$ are presented in Table 2. The representation of the experimental data by the Freundlich equation resulted in a linear curve with r values of a least 0.95 and α values <0.05 . The Freundlich model therefore appears to be a good fit of the adsorption data. In Fig. 2, the $\log(x/m)$ values represent the relative adsorption efficiency of the activated carbons and $\log C_e$, the residual concentration of the organic solutes in the treated test solution. From Fig. 2, it appears that acid-activated pecan shell-based carbon had the highest $\log(x/m)$ ratio at a given $\log C_e$ value, while the carbon dioxide-activated sample had the lowest values.

The empirical constants k and $1/n$ for both experimental and commercial carbons are given in Table 2. They are dimensionless constants that generally have meaning when compared to other values within a particular study. The values k and $1/n$ represent the intercept and slope of the adsorption isotherms in Fig. 2. Large k values indicate good adsorption efficiency for the particular activated carbon. A larger value for $1/n$ indicates a larger change in effectiveness over different equilibrium concentrations.

Generally, a carbon that has a high (x/m) value at a specified equilibrium concentration will be preferred for a given application (US Environmental Protection Agency, 1973). In this investigation, the PSA had the highest k value (15.8) followed by PSS (12.4), the commercial carbon F-200 (4.70) and PSC (1.74). Based on k values only, the adsorption effectiveness of PSA was nearly four times that of the commercial carbon, more than 12 times that of PSC and 30% more than PSS for the carbon dosages used in this study. The data in Table 2 appear to indicate that chemical activation increases k values and thereby the adsorption efficiency.

Among the three experimental carbons (PSA, PSS and PSC) and one commercial carbon (F-200), PSC had the highest $1/n$ value (1.00) followed by F-200 (0.82), PSA (0.62) and PSS (0.61). The values for $1/n$ indicate that PSC has the highest rate of adsorption of the solute and PSA and PSS the least. Therefore, while PSC can adsorb organic components more rapidly than the other carbons, it may have a more limited capacity for organic matter. Since r for all four activated carbons are greater than 0.95, and α is less than 0.05, we can assume that the graphs on Fig. 2 are linear and the Freundlich model is valid within the carbon dosage used.

Table 2
Freundlich isotherm constants for COD adsorption

Activated carbon	k	$1/n$	r	α
PSA	15.8	0.62	0.97	<0.05
PSS	12.4	0.61	0.97	<0.05
PSC	1.74	1.00	0.96	<0.05
F-200	4.70	0.82	0.96	<0.05

PSA—pecan shell acid-activated, PSS—pecan shell steam-activated, PSC—pecan shell CO_2 activated, F-200—Filtrisorb 200 (commercial carbon, bituminous coal based), n and k are dimensionless constants for the Freundlich model, r is the correlation coefficient, α is the Type I error.

6. Conclusions

Depending on the method of pecan shell activation, the resulting experimental carbons showed variations in surface area, percent attrition, pH and conductivity. The variations in surface area and percent attrition are attributed to the specific method of activation. The variations among samples for pH and conductivity are due to the extent of post activation wash treatment to remove ash components from the carbons.

The result obtained for organic matter adsorption indicates that pecan shell-based steam-activated and pecan shell-based acid-activated carbons had higher adsorptive efficiencies than the pecan shell-based carbon dioxide-activated carbon and Filtrasorb 200 at all the carbon dosages used during the experiment. These results are probably due to the differences in surface areas among the experimental and commercial carbons. Carbons with high surface area are more efficient at adsorbing the organic components in the COD sample.

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